# An Aroma Chemical Profile

# Benzyl Alcohol

By George S. Clark
Commodity Services International Inc., Easton, Maryland

Benzyl alcohol is an aroma chemical that is not an aroma chemical—maybe! The literature is awash with conflicting organoleptic terms to describe the impression of this material:

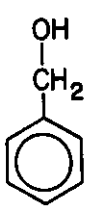
| | |
|---|---|
| Givaudan Index | Faint nondescript odor |
| Bauer/Garbe | Weak, slightly sweet odor |
| Arctander | Faint, nondescript, slightly sweet odor with a sharp taste |
| Merck Index | Faint aromatic odor, with sharp burning taste |
| Fenaroli | Pleasant, fruity odor with pungent sweet taste |
| F&FMaterials, Allured Pub. | Sweet, floral, fruity odor |
| Mosciano et al. | Odor—sweet, floral, fruity<br>Taste—chemical-fruity |

The above descriptions are only a sampling of the recorded organoleptic impressions one finds in the Flavor and Fragrance literature. A review of these sources results in an initial impact of confusion on the reader. Later on, this impression changes to the opinion that the reviewers must be examining widely different materials. Herein lies the key to benzyl alcohol's true organoleptic nature.

Freshly prepared benzyl alcohol, free from impurities, possesses a bland, aromatic impression that could be described as slightly sweet floral, damp-wet. Aged material, exposed to air, will take on a slight benzaldehyde note which, as it develops, changes the impression to fruity and then to almond as the impurities increase in trace amounts.

The material available on the market is mainly produced

**Benzyl Alcohol**




**Mwt** 108 $C_7H_8O$

**CAS** 100-51-6 **FEMA-GRAS** 2137

**Classification:**

The first of the series of aralkanols; a primary aliphatic alcohol consisting of a methylene group attached to a benzene ring.

Both FCC and NF grades are available on the world market, as well as the grade FFC (free from chlorine). Industrial grades labeled Technical and Photographic grade are also available and specifications often overlap. Often the grade is the same and the label changes.

**Additional Names:**[1-3]

| | |
|---|---|
| Phenyl carbinol | α-Hydroxytoluene |
| Phenyl methanol | Benzene methanol |

The above names are archaic and have not been used to identify benzyl alcohol for nearly 100 years.

| | |
|---|---|
| French: Alcool Benzylique | Portuguese: Alcool Benzilico |
| German: Benzyl alkohol | Spanish: Alcohol Bencilico |

**Physical Data:**[4,5]

| | |
|---|---|
| Appearance: | mobile, colorless liquid with a slight prismatic effect |
| Specific Gravity: | 1.0419 at 20°C<br>1.0413 at 25°C |
| Refractive Index: | 1.5396 at 20°C<br>1.5371 at 25°C |
| Boiling Point: | 205.4°C |
| Flash Point TCC: | 100°C |
| Solubility: | 0.08 grams in 100 grams $H_2O$. Soluble in ethanol, alcohols, esters, aldehydes, ketones, chlorinated solvents and hydrocarbons. An excellent solvent for crystalline aroma chemicals (such as musks, indol and heliotropine). |

 0272-2666/92/0006-0045$04.00/0 

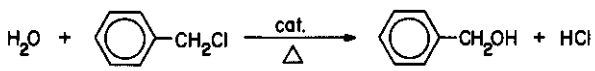



**Figure 1. Hydrolysis of benzyl chloride**

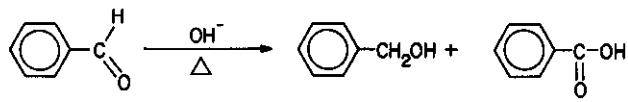



**Figure 2. The production of benzyl alcohol via the Cannizzaro Reaction**

as grades destined for industrial solvent or chemical intermediate usage. Little care is taken by the producers to manufacture an absolutely pure material, let alone one with a constant organoleptic profile. The two dominant routes of production add to the organoleptic confusion by coloring the product with their own specific impurities:

- *Mono-chlorotoluene route*: The alcohol tends to be influenced by traces of chlorine containing raw material, dibenzyl ether and oxidation products, resulting in metallic-inky, anise and almond notes in various proportions.
- *Toluene oxidation route*: This process produces material with a stronger benzaldehyde note, which is difficult to remove.

Moreover, both processes will yield redistilled material with burned-still notes, resulting from cooking the product in an attempt to remove more volatile impurities by hi-platage fractional distillation.

The overall result is that benzyl alcohol's basic bland, weak, floral-fruity note is easily colored by a number of trace impurities that create a number of grades, and vary considerably from batch to batch, with any given process. That is why the literature contains confusing reports which indicate organoleptic descriptions that appear to be contradictory.

With these problems noted, we can address the question of whether benzyl alcohol is an aroma chemical or just a solvent. However, the answer is amorphous rather than as clear as heads or tails in the toss of a coin.

In fragrances, benzyl alcohol is used mainly as a solvent for certain crystalline aroma chemicals, such as musks, but also as a modifier of odor in some flower compositions, such as jasmine, where it is found in the essential oil of the flower. Its ability to tone the notes of other constituents in floral compositions places it in the general area of hydroxycitronellal (although this material contributes more odor impact in formulations).

In flavors, again benzyl alcohol is used as a solvent, but also is added to modify certain flavor compositions, especially berry and fruit formulas, where it contributes organoleptically.

However, in no instances can it be said that benzyl alcohol was added to a flavor or fragrance because its individual organoleptic impression was a key determinant of the formula concept. In this respect benzyl alcohol is more of a solvent than an aroma chemical, but the argument is one of degree rather than classification.

## Natural Sources

Benzyl alcohol is found in a fair number of natural products used and consumed by humans worldwide. World consumption via food stuffs is estimated at about 16,000 kg of natural benzyl alcohol per year, while the contribution of essential oils for fragrances adds only about 4,000 kg to the total presence of natural benzyl alcohol; bringing the total usage in the flavor and fragrance industry to about 20,000 kg per year of natural benzyl alcohol.

In the fragrance area benzyl alcohol has been reported as a minor constituent in the following essential oils:

| | |
|---|---|
| basil | jasmine |
| cassie (acacia) | hyacinth |
| ylang-ylang | chervil |
| Peru balsam | clove |
| tolu balsam | mandarin |
| storax | rose |
| neroli | Siberian fir needle |
| tuberose | Prunus mume |
| orris | Daphne odora |
| castoream | violet leaves |
| wall flower | |

In the food/flavor area, benzyl alcohol has been reported as a minor constituent in the following products:

| | |
|---|---|
| bread | raspberry |
| cocoa | strawberry |
| apples | tea |
| apple juice | wine |
| cranberries | tobacco |
| chicken (cooked) | grapes |
| mushrooms | peaches |

In no case is benzyl alcohol present in more than trace to minor amounts; nor can its presence be considered a major determinant of the taste or odor profile of the natural product in which it is found.

## History

The history of benzyl alcohol is intertwined with that of benzaldehyde. Both were dependent upon developments in the coal tar and dye industry during the 1800s. The need for benzyl chloride in dye synthesis sparked the research into its synthesis via the chlorination of toluene to yield benzyl chloride, benzyl dichloride and benzyl trichloride, and then to devise routes to improve the hydrolysis[6] of these products into benzyl alcohol, benzaldehyde and benzoic acid.

In 1853, Cannizzaro reported that benzaldehyde would react to caustic and break into equal quantities of benzyl alcohol and benzoate salts.[10] By 1904 these two production

**Table I. Major producers of benzyl alcohol, along with the synthetic routes**

| Firm | Process |
|---|---|
| Akzo | benzyl chloride |
| Bayer | benzyl chloride |
| China (Shanghai Native Produce) | benzyl chloride |
| DSM | benzaldehyde |
| Kalama Chemicals | benzaldehyde |
| Quest | benzyl chloride |
| Marlborough (MTM) | benzyl chloride |

**Table II. Estimated consumption of *benzyl alcohol for 1992***

| Area | MT/Year |
|---|---|
| Chemical Intermediate Usage | 13,400 |
| Industrial | 7,400 |
| Aroma Chemicals (benzyl acetate) | 6,000 |
| Photographic Usage | 2,000 |
| Flavors and Fragrances (direct use) | 600 |
| **Total consumption** | **16,000** |

methods were so basic to the chemical industry that the two reactions were included in college laboratory experiments in order to train chemists.[7] Thus, these two reactions provided then, as they do today, the two major routes for the commercial production of benzyl alcohol.

Prior to 1914, the production of benzyl alcohol was solely in the hands of European dye manufacturers, where its major use was as a solvent for dyes, and most of that activity was carried out in Germany. The isolation of the US from its European chemical sources during World War I resulted in a rapid rise of the US synthetic organic chemical industry. Benzyl chloride production began domestically as did the production of benzyl alcohol and benzaldehyde, again mainly by synthetic dye stuff manufacturers.

The 1920s saw the founding of small specialty aroma chemical firms such as Harold Simmons Inc. and George Fries,[8] which began manufacturing benzyl alcohol and other aroma chemicals to fit the organoleptic needs of the F&F industry as the products of most chemical manufacturers were too crude to be used.

In the 1930s, Trubek became involved with the manufacture of these products as well as Fritzsche, Norda and Givaudan. The consolidation of firms after World War II and the improvement in industrial benzyl alcohol quality resulted in a gradual suspension of production of benzyl alcohol by aroma chemical suppliers. Thus began the practice of reselling selected lots purchased from industrial chemical producers.

Eventually, the industrial chemical producers attempted to sell flavor and fragrance grade benzyl alcohol directly to F&F houses with mixed success. This evolution has continued so that the dominant manufacturers of benzyl alcohol today are not aroma chemical suppliers but industrial chemical firms. The improvement of processes and equipment over the past 30 years has resulted in usable F&F grade benzyl alcohol becoming available as selected lots of industrial grade material, rather than repurified and redistilled commercial grades offered by F&F houses in the past.

The last 20 years have seen changes in the use pattern for industrial benzyl alcohol and decreased world production volumes. Its industrial usage in the Dye area has largely ceased due to waste disposal considerations. The sudden large requirements for the production of aspartame seen in the early 1980s disappeared in 1989, eliminating about 30% of the world demand. The end result of these market changes has been a consolidation of supply and fewer manufacturers.

## Synthetic Routes and Producers

The dominant synthetic route for the commercial production of benzyl alcohol today is the hydrolysis of benzyl chloride (Figure 1), as it provides a cleaner, purer product void of critical off odors. Various catalytic systems have been developed to accelerate the rate of conversion of benzyl chloride and to steer the reaction to the best yields.[9]

The production of benzyl alcohol via the Cannizzaro Reaction (Figure 2) is only practiced by few manufacturers today, as it yields product invariably contaminated with traces of benzaldehyde, which hinders its use in flavors or fragrances. Most producers are using benzaldehyde as a feed stock catalitic hydrogenation for the reduction to benzyl alcohol, however, the organoleptic problem is the same as the basic Cannizzaro Reaction.

The major world producers of benzyl alcohol and their synthetic routes are presented in Table I.

## Capacity/Supply

The total world production of benzyl chloride is in excess of 200,000 MT/year and current benzyl alcohol production is estimated at 16,000 MT/year. Of the 16,000 MT/year of world production of synthetic benzyl alcohol, it is estimated that no more than 600 MT is consumed directly (as is) in both flavors and fragrances worldwide.

In general the plant equipment used to convert benzyl chloride to benzyl alcohol is dedicated mono production units. Both current use capacity, as well as design capacity, are well in excess of demand by more than 50%.

The only apparent limitation seen for F&F-grade benzyl alcohol is the organoleptic variations in the current in-place processes, as the large part of world production of benzyl alcohol yields material too highly colored by impurities to be usable in our industry.

## World Consumption

Of the 16,000 MT of worldwide benzyl alcohol production, the consumption areas are estimated as listed in Table

II. The usage by geographic location in the flavor and fragrance industry is given in Table III.

**Table III. Estimated usage of benzyl alcohol in flavor and fragrance industry (in MT)**

| Area | Direct Use in F&F | Aroma Chemical Intermediate |
|---|---|---|
| North America | 150 | 200 |
| Europe | 200 | 2,700 |
| Asia | 180 | 2,000 |
| Latin America | 50 | 975 |
| Others | 20 | 125 |
| **Total** | **600** | **6,000** |

## Imports

Benzyl alcohol is listed under TSUS 2906.2100006 and bears a nominal duty of 6.6% ad valorum, a duty level which does little to prevent importation of the product. Thus, most of the benzyl alcohol used in the US today is imported.

## Pricing

Figure 3 presents the average price of benzyl alcohol (all grades) in the US$/lb for the US market during the period 1974 through 1992. The sharp fluctuations in the 1974 to 1978 period were due to sporadic foreign competition, tariff changes, and the emerging use of benzyl alcohol as a protective group in the production of l-phenylalanine for use in aspartame. This growing usage placed capacity loads on world production that resulted in steadily rising prices from 1977 to 1988. When the process changes for the production of aspartame eliminated the demand, world prices rapidly fell to about half of their 1988 highs. It is estimated that aspartame production consumed 30% of world benzyl alcohol product at its peak.

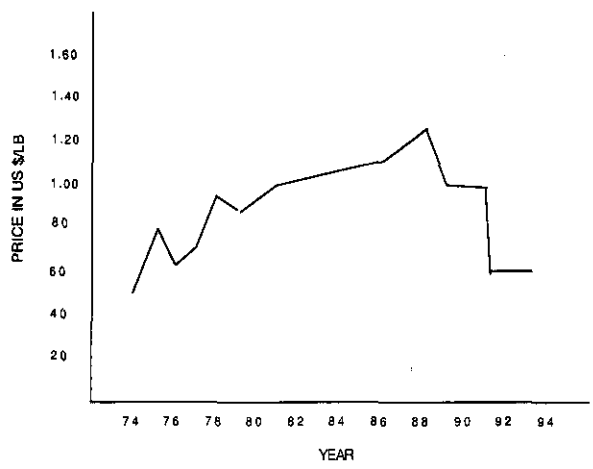
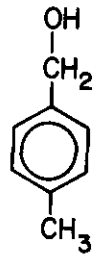



**Figure 3. Prices of benzyl alcohol from 1974 to 1992**




[I]
Arct 2958

**Figure 4. p-Tolyl alcohol**
(Arct = Arctander's number)

## Substitutes

The question of substitutes for a large-volume industrial chemical priced at very low market values is more of an academic exercise than a practical one. Certainly the aralkanol most similar in chemical properties and organoleptic profile would be p-tolyl alcohol [I] (Figure 4). However, this material is more difficult to obtain and bears much higher pricing. Substituting benzyl alcohol for its solvent properties would dictate the selection of DMP (dimethyl phthalate) or DEP (diethyl phthalate) or benzyl benzoate in fragrances as well as the solvent used in flavors. In the flavor area diacetin, triacetin, triethyl citrate, or propylene glycol can be used as solvent sub-

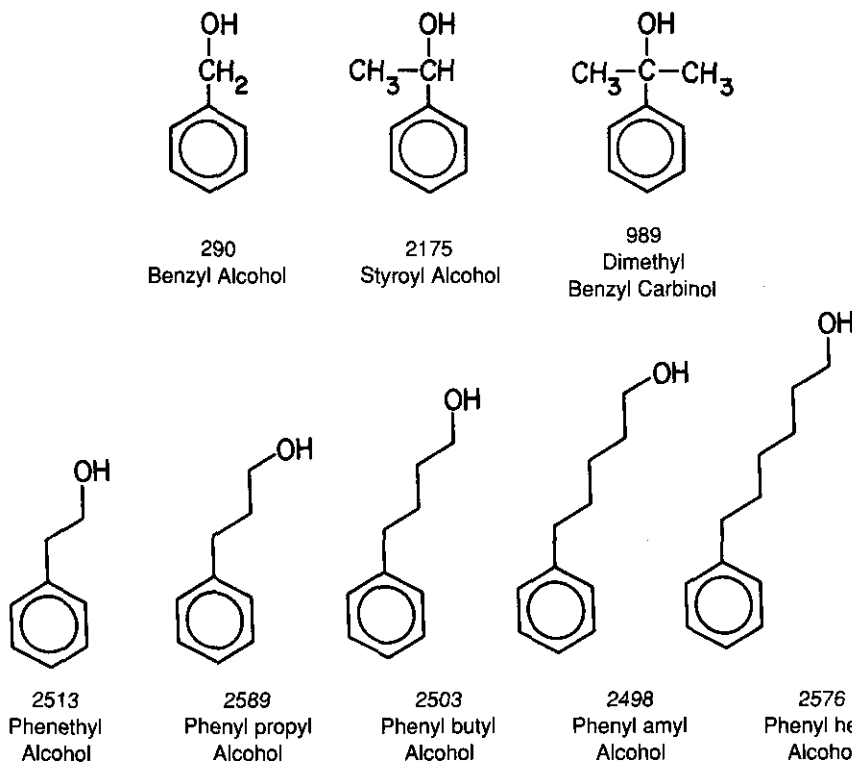



**Figure 5. The chief analogues of benzyl alcohol** *(numbers refer to Arctander's work)*

stitutes depending on the products requiring solvation.

## Analogues

The analogues of benzyl alcohol (Figure 5) all have more merit for use in flavors or fragrances, than this alcohol which is first in the aralkanol series. These analogues in varying volumes all find use in the flavor and fragrance industry, as do their esters, particularly the acetates and butyrates. Certainly phenyl ethyl alcohol is one of the workhorses of our industry.

## Derivatives

The products listed below are generally available to the flavor and fragrance trade from commercial sources and convey the importance of this group of materials to the industry.

| Chemical | GRAS/FEMA # |
|---|---|
| benzyl acetate | 2135 |
| benzyl aceto acetate | 2136 |
| benzyl anthranilate | ---- |
| benzyl benzoate | 2138 |
| benzyl butyl ether | 2139 |
| benzyl butyrate | 2140 |
| benzyl caprylate | ---- |
| benzyl cinnamate | 2142 |
| benzyl disulfide | 3617 |
| benzyl ethyl ether | 2144 |
| benzyl formate | 2145 |
| benzyl isoamyl ether | ---- |
| benzyl isobutyrate | 2141 |
| benzyl isovalerate | 2152 |
| benzyl mercaptan | 2147 |
| benzyl trans-2-methyl-2-butenoate | 3330 |
| benzyl n-valerate | ---- |
| benzyl phenyl acetate | 2149 |
| benzyl propionate | 2150 |
| benzyl salicylate | 2151 |
| benzyl ether | 2371 |

### References

Address correspondence to George S Clark, Commodity Services International, Inc, PO Box 1876, Easton MD 21601 USA.

1. S Arctander, *Perfume and Flavor Chemicals* (1969) No 290
2. *The Givaudan Index*, 2nd Ed, Givaudan Delwanna, Inc (1961) p 69
3. *Merck Index*, No 1130, 10th Ed (1983)
4. K Bauer and D Garbe, *Common Fragrances and Flavor Materials*, Weinheim, Germany: VCH Press (1985) p 64
5. J Dean, *Lang's Handbook of Chemistry*, 13th Ed, McGraw-Hill (1985) pp 7137 and 6112
6. Meunier, *Bull Soc Chim* (2) 38 (1882) p 159
7. E Fisher, *Anleitung zur Darstellung Organischer Praeparate*, F Vieweg and Sohn Verlag, Braunschweig, Germany (1905) pp 29-31
8. W Dorland and J Rodgers, *The Fragrance and Flavor Industry*, WE Dorland Co (1977)
9. PZ Bedoukian, *Perfumery and Flavoring Synthetics*, 3rd Ed, Allured Publ Corp, Wheaton, IL (1986) p 62
10. S Cannizzano, *Libigs Ann Chem* **88** 129 (1853)